Covalency in Oxidized Uranium

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Abstract

Using X-ray Emission Spectroscopy (XES) and Absorption Spectroscopy (XAS), it has been possible to directly access the states in the unoccupied density of states (UDOS) that are involved with 5f and 6d covalency in oxidized Uranium. By varying the oxidizing agent, the degree of 5f covalency can be manipulated and monitored.

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Introduction

Actinides, the 5f elements and their compounds, alloys and mixtures, are a crucially important part of modern technological societies. [1] While holding forth the promise of low-carbon-footprint energy, there are corresponding massive problems associated with them, ranging from environmental clean-up [2] to long term radiological storage [3]. In the USA, nuclear power provides for 20% of the national electrical grid [1]. For many counties in Europe, the percentage is substantially higher [1]. Uranium dioxide is the most widely used fuel for the generation of electricity [1]. Yet, because of the complexity of the 5f/6d electronic structure in the actinides, a fundamental understanding of their physical behavior has not been achieved.

Theoretically, it has been proposed that covalency is an important part of the electronic structure of actinide dioxides [4], although not everyone agrees [5]. Experimentally, spectroscopic studies have been reported, by these authors, which support this hypothesis [6,7]. However, an important component has been missing: a systematic study where the nature of the oxidant is changed, so the specifics of the 5f and 6d covalencies could be varied and monitored. Herein is reported such a study.

Fluorine is very reactive and dangerous material [8]. It's halogen cousins, chlorine and iodine, have common usage as oxidizing agents amongst the general population: e.g. in swimming pools and clean wipes for chlorine; and water purification and wound disinfectant for iodine. However, fluorine's propensity to oxidize is so strong that it ends up being used in applications such as rocket fuel.

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Moreover, it has a very dangerous side and can be a threat to human well-being. For example, hydrofluoric acid is a known bone-seeker, often leading to amputations.

Thus, this comparative study will feature the isoelectronic systems uranium dioxide (UO_2) and uranium tetrafluoride [UF_4]. While isoelectronic, both being U^{+4} $5f^2$ in the formal limit [9], they exhibit substantially different structures. UO_2 is a fluorite (cubic) material, while UF_4 is monoclinic: however, both exhibit very similar U L_3 extended x-ray absorption fine structure (EXAFS) behavior, indicative of similar bond lengths [10]. UF_4 has been studied before with X-ray absorption [11], but these measurements are complimentary to the earlier study (e.g. F1s XAS), and have been performed with improved resolution and over a more extensive energy range (e.g the U L_3 X-ray absorption fine structure or XANES and EXAFS) [10,12]. The result of this comparative study is that UF_4 exhibits continued 6d covalency but the almost complete loss of 5f covalency, while UO_2 clearly displays both strong 5f and 6d covalencies. 5f covalency is important in actinide oxides, but can be lost with a more powerful oxidizing agent such as F.

Experimental

The x-ray measurements were performed upon three beamlines: BL 8.0 at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL) in Berkeley, CA; BL 6-2 and BL 11-2, both at the Stanford Synchrotron Radiation Lightsource (SSRL) in Palo Alto, CA. For BL 8.0, energy calibrations were performed at the Fe $2p_{3/2}$ white line (710 eV for iron oxide) for the beamline monochromator and at the F1s (at 675 eV [1]) for the fluorescence monochromator and detector. Details of the BL 8.0 characteristics can be found in Ref. 13. The

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Partial Fluorescence Yield (PFY) L_3 XAS [14,15] data were collected at SSRL wiggler

beamline 6-2 using an LN_2-cooled Si (331) double monochromator calibrated so

that the inflection point of a UO_2 reference was at 17166.0 eV. The emission energy

was measured using a seven-crystal Ge(777) Johann-type X-ray emission [16]

spectrometer, at an emission energy of approximately 13.6 keV, corresponding to

the U $L_{\alpha 1}$ edge.   Data were collected at room temperature (300 K). The resolution

was 1.4 eV at the U $L_{\alpha 1}$ emission energy. The "regular" XAS U L_3-edge data [10] were

collected in fluorescence mode from the U $L_{\alpha 1}$ line on BL 11-2 at SSRL, with a half-

tuned double Si(220) (ϕ = 0°) LN_2-cooled monochromator on unfocused beam and a

100-element Ge solid-state detector [17], with the sample at T = 50 K.   The effective

line-width in the "regular" XANES measurements is on the order of 10 eV, much

greater than the PFY XANES above. The uranium dioxide sample used in Reference

7 was polycrystalline with a well-defined surface [1,6,7]. The uranium tetrafluoride

was a single crystalline sample, with significant surface degradation [1].

Results and Discussion

In two earlier studies, strong evidence of 5f and 6d covalency was found in

UO_2. First, XAS was used to show that the unoccupied states of uranium and oxygen

overlapped in a significant way, suggesting that that there was both U5f-O2p

hybridization and U6d-O2p hybridization[6].   Second, a detailed study with

Resonant Inverse Photoelectron Spectroscopy (RIPES) was performed, which

provided another confirmation of the splitting of the uranium UDOS into two sub-

bands, for the U5f and U6d states. Moreover, it was found that the U4d XES

provided essentially the same information, without the limitation of the strong

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surface sensitivity of RIPES. While the decay process of XES provides a measure of

the Occupied Density of States (ODOS), *it is the ODOS in the presence of a core hole*.

Thus, because changing the effective nuclear charge in the actinides can shift

energies by 10's of eV [1], the original low lying UDOS were now occupied and the

4d XES provided a measure of the original low-lying UDOS. These results are

summarized in Figure 1.

To extend the measurements to UF_4, an operational change was necessary.

While the UO_2 sample used in Reference 7 had a well-defined and clean surface, the

UF_4 sample would not be thus. It is possible to sputter clean the surface of a UF_4

sample, but then the stoichiometry would be ruined.   Rather than change the

stoichiometry, it was decided to probe the UF_4 only with spectroscopies that could

sample bulk behavior. For example, as reported earlier, while X-ray Photoelectron

Spectroscopy (XPS) could only see uranium, oxygen and carbon on the surface of the

UF4 sample, the F1s XES was clearly and strongly visible. Interestingly, it is

important that there is little or no F on the surface: This means that the F signal will

be coming from the bulk. This issue will be revisited later.

Consider the spectra in Figure 2. In the top panel, there is the XES for the

detector photon energy region of 660 eV to 760 eV, using an excitation-photon-

energy of 800 eV. The detector energy here is calibrated upon similar

measurements made in-house of the F1s XES [1]. The F1s peak is strong and well

defined, very similar to the F1s peak in Reference 1. The U4d peak, shown in the

blow-up, is at least three orders of magnitude weaker, but still visible above the

noise. Clearly, there is only one major peak here, already different than the result

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for uranium dioxide. Because the XPS showed no surface peak, it is safe to conclude that the F1s XES is solely derived from the bulk. It is important that the F1s and U4d features were collect in one scan, eliminating the issue of energy calibration for an isolated U4d peak. While time consuming (8- 12 hours), it permits the overlay of peaks that will be utilized below. Similarly, a wide XAS spectrum was collected for the uranium tetrafluoride, shown in the middle panel. Here the energy calibration is based upon the Fe2p of iron oxide, which can be seen in both the I_0 and Total Electron Yield (TEY) Curves. TEY is fairly surface sensitive: the poor quality of the TEY is a reminder and confirmation of the corrosion of the outside of the uranium tetrafluoride sample. This can be further confirmed by looking at the O1s XAS of the UF4 sample, shown in an insert in the upper right corner. There shouldn't be any oxygen in the uranium tetrafluoride, so the presence of any O1s intensity is indicative of surface corruption. Moreover, the three peak spectral structure is reminiscent of the O1s spectra of UO_3 of Magnussen et al [18] or the $(AcO_2Cl_4)^{-2}$ uranyl compounds, reported by Minasian, Clark and others [19], not at all like our O1s from uranium dioxide, also shown in the corner inset. Thus, some of the corrosion may be in the form of UO_2F_2 or UO_3 or an analogous uranyl structure. In contrast to the surface sensitive TEY, the Total Fluorescence Yield exhibits a plethora of fine structure, which is all easily understandable. As with the XES, the TFY measurements are all photon and thus bulk sensitive. One can clearly see the detailed spectral features near the F1s threshold near 690 eV. There are also Extended X-ray Absorption Fine Structure features that continue throughout. The F1s EXAFS is the same as the UL_3 EXAFS, shown in the bottom panel of Figure 2,

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although the F1s leads the UL$_3$ by 90 "degrees" [20]. Because the phase relationship

holds in k-space, the relationship gets distorted in energy space, but it is obvious

nonetheless. It is also worth noting that the F1s EXAFS from UF$_4$ and the O1s EXAFS

from UO$_2$ are very similar, paralleling the strong similarities in their L$_3$ EXAFS [10].

There should be U4d$_{5/2}$ XAS (about 736 eV) and U4d$_{3/2}$ XAS (about 778 eV) [11,12].

However, as suggested by the XES results, these peaks will be small relative to the

F1s XAS. Moreover, all of the uraniums will contribute, thus broadening the already

weak features but shifts from the chemical inhomogeneity of the different forms of

uranium. Thus, the likelihood of seeing a U4d XAS peak is small, and instead, these

will manifest themselves as broadening in the F1s EXAFS. It should also be noted

that the strong F1s EXAFS is supportive of the contention that the F1s intensity is

bulk derived, being so clearly associated with the L$_3$ EXAFS from bulk uranium

fluoride. Next, the data from these measurements will be overlayed in a fashion

similar to the data in Figure 1.

Consider now the overlay of spectra in Figure 3, for the uranium

tetrafluoride sample. To align the XAS spectra, we used the threshold method,

developed earlier for uranium dioxide [6]. Here, instead of using the low energy 4f

XAS to access the 6d UDOS, the bulk sensitive L$_3$ (2p$_{3/2}$) XAS has been utilized. Again,

this method is dependent upon the dominance of electric dipole selection rules, as in

Reference 6. The energy scale on the lower panel is determined by that used in the

analysis of the uranium dioxide [1,7] and the alignment of the F1s peaks in the in

house and ALS experiments and the utilization of the inclusive wide scan in Figure 2.

The U4d XES was measure at several excitation energies, always producing the

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result of a single, fairly strong peak. Shown in Figure 3 are data that were collected

at hv_{EX} = 722 eV, with an extended data collection period to reduce the noise. This

energy is seemingly below threshold, but as reported earlier [1], the wide lifetime

broadening in these XES events permits excitations with lower energies. Under

these conditions, there appeared a second but very weak feature at about 735 eV.

This feature matches perfectly with the reduced peak in the F1s XAS, suggesting that

the U5f-F2p hybridization has been reduced relative to the U5f-O2p hybridization in

the uranium dioxide. Note that the major peaks in both the F1s XAS and the U4d

XAS have shifted together, retaining their overlap. This suggests that the U6d-F2p

hybridization remains intact. (The U6d driven peak in the U4d XES is driven by a

two electron process, discussed in References 1 and 7.) This hypothesis is

confirmed by the placement of the U2p XAS, in the vicinity of the the main F1s XAS

and U4d XES peaks.

At this point, it is useful to look at the internal structure of the UL_3 peak. This

has been done in detail in Reference 12 for both UO_2 and UF_4, so here only the

pertinent aspects will be summarized. Cluster calculations by Ryzhkov et al provide

a histogrammatic UDOS for uranium tetrafluoride and uranium dioxide [21,22].

Using Doniach-Sunjic lineshapes [23] and assuming equal intensities, the smaller

yellow curves are generated as shown in Figure 3, along with the sum shown as the

larger broader curve. Clearly, some of these 6d states in the UDOS fall directly

below the F1s XAS main peak and above the U4d XES main peak, thus confirming

the assignment as U6d-F2p hybridization.

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By changing the oxidizing agent, it is possible to enhance (UO_2) or diminish (UF_4) the U5f-2p hybridization. The highly electronegative F drives the system tords ionic behavior, while the dioxide exhibits strong U5f-O2p hybridization. The U6d-2p hybridization persists, even in the ionic UF_4. Further, there is an important application to more highly radioactive samples here: the 4d XES is feasible with either photon or electron excitation, so in-house experiments upon highly radioactive Np, Pu and Am samples are possible. The relative magnitude or the two U4d XES features can provide a direct measure of 5f-2p hybridization versus 6d-2p hybridization, without the need to take highly radioactive samples to synchrotron radiation light sources.

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References

1. S.-W. Yu and J.G. Tobin, J. Electron Spectroscopy Rel. Phen. **187 ,** 15 (2012) and references therein.

2. I.L. Pegg, Physics Today **68**, 33 (2015).

3. M.L. Wald, The New York Times, page A20, October 17, 2014.

4. I.D. Prodan, G.E. Scuseria, R.L. Martin, Phys. Rev. B **76,** 033101 (2007).

5. L. Petit, et al., Phys. Rev. B **81** 045108 (2010).

6. S.-W. Yu, J. G. Tobin, J. C. Crowhurst, S. Sharma, J. K. Dewhurst, P. Olalde-Velasco, W. L. Yang, and W. J. Siekhaus, Phys. Rev. B **83**, 165102 (2011).

7. J.G. Tobin and S.-W. Yu**,** Phys. Rev. Lett, **107,** 167406 (2011).

8. Fluorine, http://en.wikipedia.org/wiki/Fluorine.

9. J. Tobin, J. Electron Spectroscopy Rel. Phen. **194 ,** 14 (2014).

10. J.G Tobin, C.H. Booth, W. Siekhaus and D.K. Shuh, "EXAFS Investigation of UF_4," J. Vac. Sci. Tech. A, accepted March 2015.

11. G. Kalkowski, G. Kaindl, W.D. Brewer and W. Krone, Phys. Rev B **35**, 2667 (1987).

12. JG Tobin, S.-W. Yu, CH Booth, T. Tyliszczak, DK Shuh, G. van der Laan, D. Sokaras, D. Nordlund, T.-C. Weng, and P.S. Bagus, "Oxidation and Crystal Field Effects in Uranium," under preparation.

13. J. J. Jia, T. A. Callcott, J. Yurkas, A. W. Ellis, F. J. Himpsel, M. G. Samant, J. Stohr, D. L. Ederer, J. A. Carlisle, E. A. Hudson, L. J. Terminello, D. K. Shuh, and R. C. C. Perera, Rev. Sci. Instrum. **66**, 1394 (1995).

14.   C.H. Booth, Yu Jiang, D.L. Wang, J.N. Mitchell, P.H. Tobash, E.D. Bauer, M.A. Wall, P.G. Allen, D. Sokaras, D. Nordlund, T.-C. Weng, M.A. Torrez, and J.L. Sarrao, Proc. Natl. Acad. Sci. **109**, 10205 (2012).

15.   C.H. Booth, S.A. Medling, Y. Jiang, E.D. Bauer, P.H. Tobash, J.N. Mitchell, D.K. Veirs, M.A. Wall, P.G. Allen, J.J. Kas, D. Sokaras, D. Nordlund, T.-C. Weng, J. Electron Spectroscopy and Rel. Phen. **194** 57 (2014).

16.   P. Glatzel and U. Bergmann, Coord Chem. Rev. **249**, 65 (2005).

17.   J. J. Bucher, P. G. Allen, N. M. Edelstein, D. K. Shuh, N. W. Madden, C. Cork, P. Luke, D. Pehl, and D. Malone, Review of Scientific Instruments **67**, 3361 (1996).

18.   M. Magnuson, S.M. Butorin, L. Werme, J. Nordgren, K.E. Ivanov, J.-H. Guo , D.K. Shuh, Applied Surface Science **252**, 5615(2006).

19.   D.L. Clark, "Chemical Bonding in Molecules with Valence 5f Electrons," SESTEC 2014 International Conference, Mumbai, India, February 2014, LA-UR-14-20496.

20.   B.K. Teo, "EXAFS Basic Principles and Data Analysis," Springer Verlag, New York, 1986.

21.   Yu. A. Teterin, K. I. Maslakov, M. V. Ryzhkov, O.P. Traparic, L. Vukcevic, A. Yu. Teterin, and A. D. Panov, Radiochemistry **47**, 215 (2005).

22.   A. Yu. Teterin, Yu. A. Teterin, K. I. Maslakov, A. D. Panov, M. V. Ryzhkov, L. Vukcevic, Phys. Rev. B **74**, 045101 (2006).

23.   J.G. Tobin and F.O. Schumann, Surface Science **478**, 211 (2001).
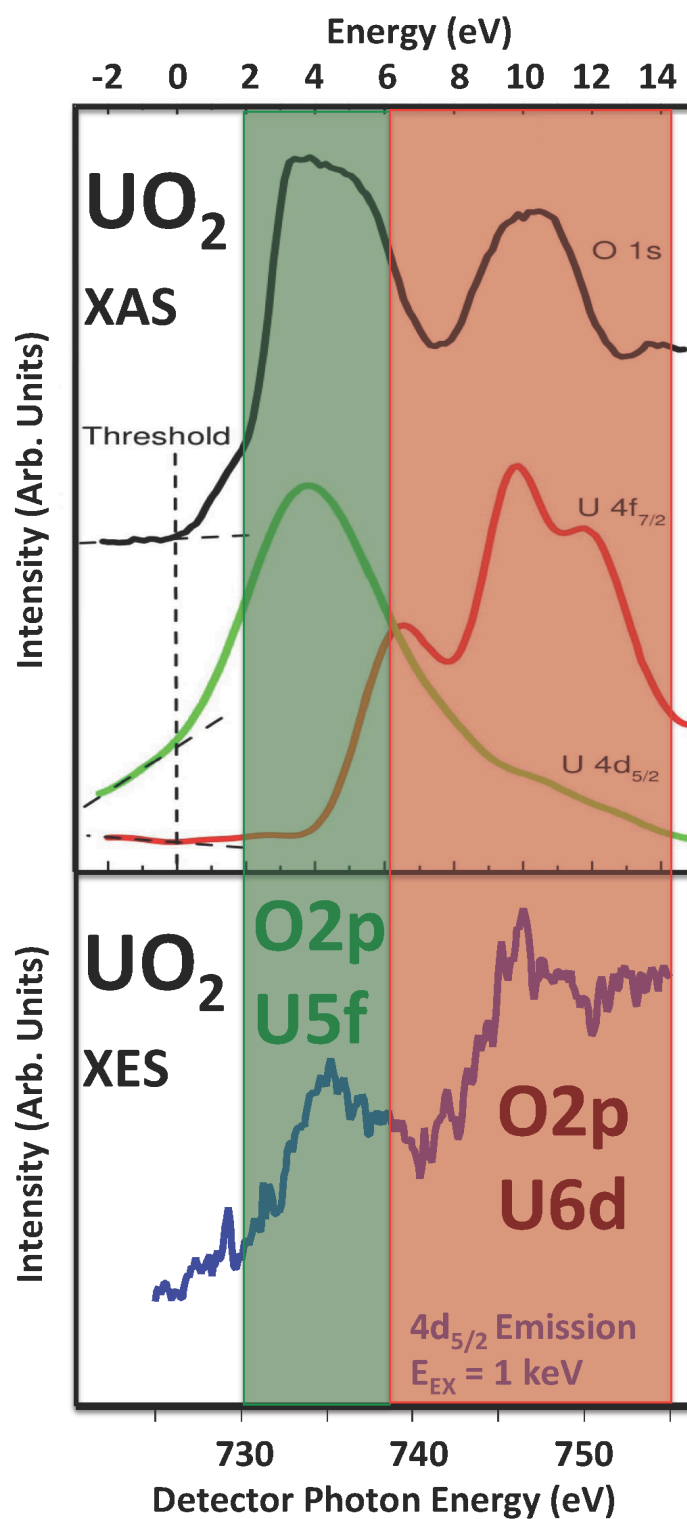
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Figure 1
The Unoccupied Density of States (UDOS) of UO_2, as determined from the O1s, U4f and U4d XAS and the U 4d XES is shown here. See text for details. Here, the XES is performed in house, using an electron gun for excitation. [7]
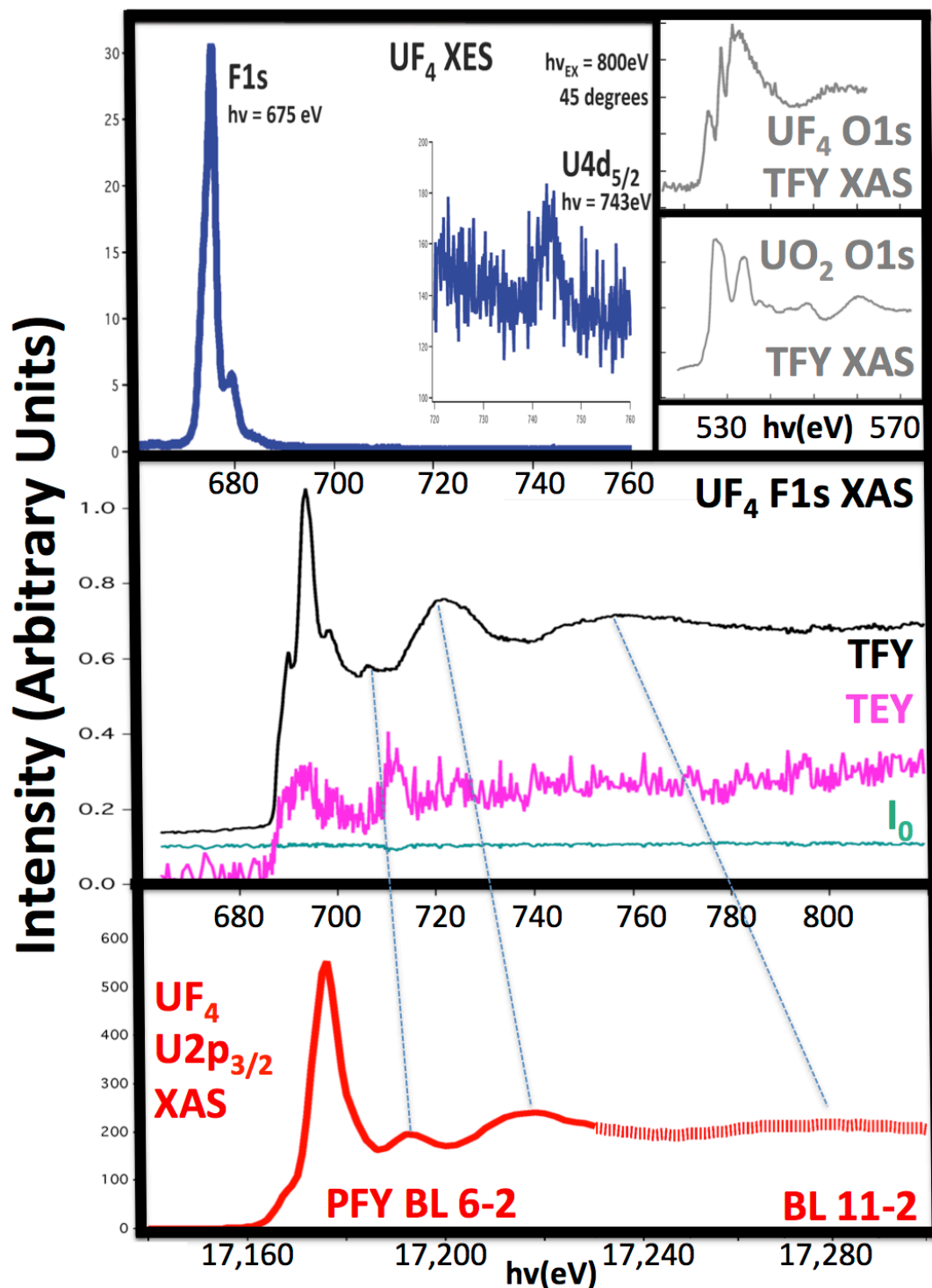
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Figure 2
The XES and XAS of UF₄, plus supporting measurements, are displayed here. See text for details. The solid part of the U2p data is from Beamline 6-2 [12] ; the dashed from Beamline 11-2 [10]. TFY is total fluorescent yield. TEY is total electron yield. I_0 is a measure of the beamline photon intensity.
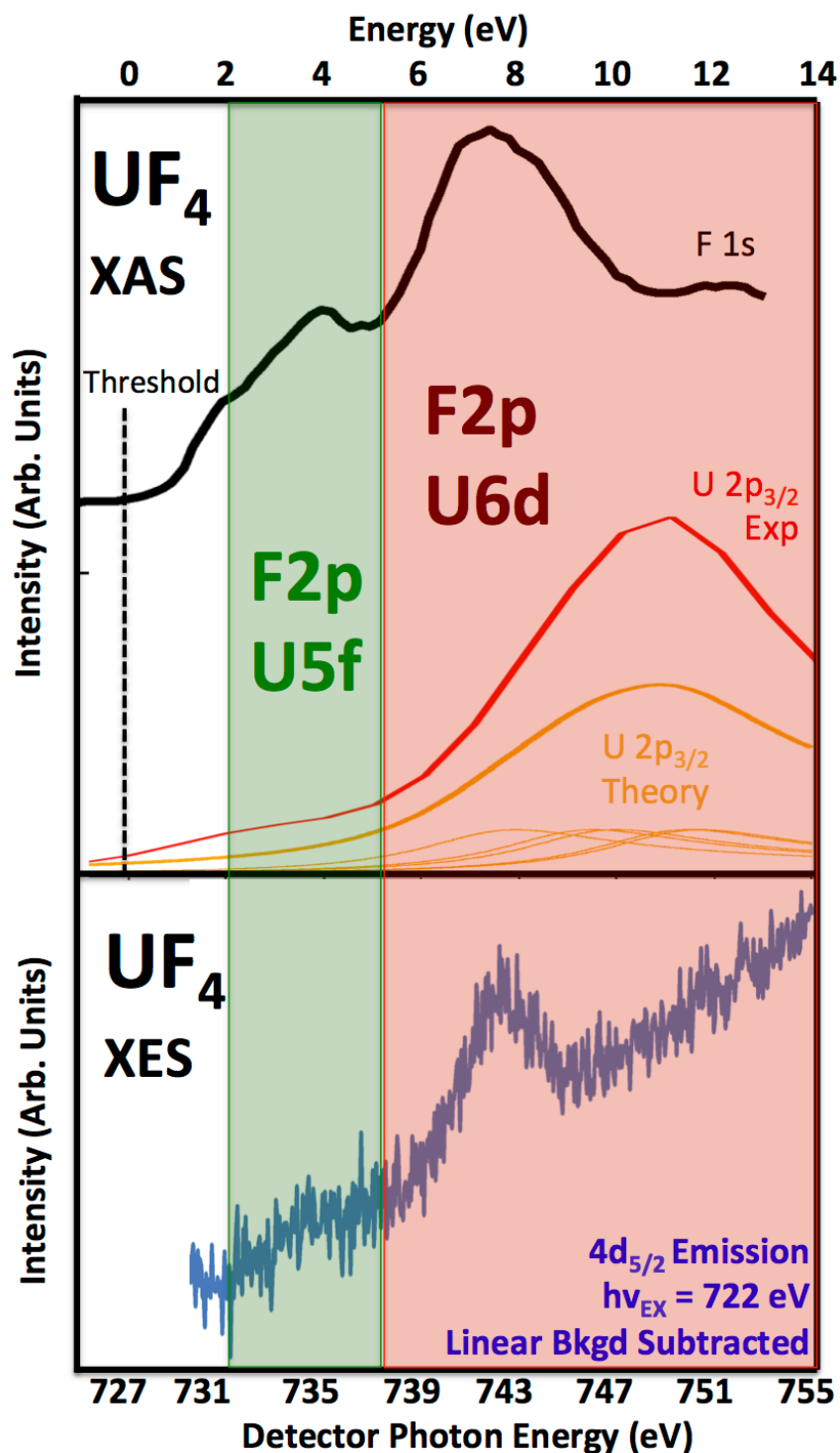
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Figure 3
The Unoccupied Density of States (UDOS) of UF4, as determined from the F1s and U2p XAS and the U 4d XES is shown here. A simulated U2p spectrum is also included, with the underlying states from the Ryzhkov cluster calculations. See text for details.